KMITL Sci. Tech. J. Vol. 16 No. 2 Jul.-Dec. 2016

# Effect of Oxygen Plasma on Tin Oxide Nanorods Prepared by GLAD Technique

Chaiyan Oros*

Faculty of Liberal-arts, Rajamangala University of Technology Rattanakosin, Nakornpathom, Thailand

## Abstract

In this work, the effect of oxygen plasma with varing plasma power from 100 W to 300 W on tin oxide ($SnO_2$) nanorods prepared by glancing angle deposition (GLAD) technique was studied. The crystal structures were characterized by X-ray diffraction (XRD) technique and the morphology was characterized by field-emission scanning electron microscopy (FE-SEM) technique. Atomic-force microscopy (AFM) revealed that the as-deposited and oxygen plasma-treated tin oxide nanorod structures had orthorhombic phase of $SnO_2$. The degree of crystallinity tended to improve as the plasma power increasd from 100 W to 300 W In addition, the surface roughness of tin oxide nanorods increased with oxygen plasma power increasing. However, the thickness decreased with oxygen plasma power increasing.

**Keywords:** Oxygen plasma, tin oxide nanorods, GLAD technique

## 1. Introduction

Tin oxide ($SnO_2$) is a material widely used in mechanical surface coating, transparent conducting electrodes, solar cells and semiconductor gas sensors. It is a n-type semiconductor with a wide band gap (3.6 eV) and a rutile structure. Tin oxide based gas sensors are of particularly interesting due to their high stability and high sensitivity to a broad range of gases at relatively low operating temperatures. The performances of metal oxide gas sensors directly depend on the surface and morphology of the active material. Many studies have shown that the metal oxide semiconductor structure with a high surface to volume ratio would provide superior gas-sensing performance. Recently, high-sensitivity gas sensors based on crystalline nanostructures, i.e. nanowire, nanotube or nanorod of tin oxide have been demonstrated [1-3]. Tin oxide might be prepared by various methods including evaporation, sputtering, chemical vapor deposition and sol gel processes. These methods mostly produce random $SnO_2$ nanostructures, which are not desirable for commercial applications. Practical techniques for well-ordered nanostructure construction are thus needed.

*Corresponding author: E-mail: Chaiyan.Oro@rmutr.ac.th

Glancing angle deposition (GLAD), also known as oblique angle deposition, is a method to grow well ordered nanostructures such as nanorods, nanosprings, zigzag columns, etc. [4-5]. It is a physical vapor deposition technique, in which a high melting point material flux is incident onto the substrate from a glancing angle (α), which is typically, greater than 80° so as to exacerbate atomic shadowing effects. Low surface mobility of adatoms lead to kinetic limitations such as geometrical confinements and atomic shadowing, resulting in the formation of a variety of porous columnar microstructures [6-7]. In this work, tin oxide nanorods was prepared by glancing angle deposition (GLAD) technique using a reactive DC magnetron sputtering process and the effect of oxygen plasma with varying plasma power from 100 to 300 watt on tin oxide ($SnO_2$) nanorods formation is studied [8-9]. Structural Characterization was performed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Atomic-force microscopy (AFM).

## 2. Experimental

Tin oxide nanorods were fabricated by a DC reactive magnetron sputtering system using GLAD technique as schematically illustrated in Figure 1. The distance from the target to substrate center and the substrate rotation speed were fixed at 7 cm and 5 rpm, respectively. The substrate normal was positioned at an angle of 85° ($\alpha$ = 85°) with the respect to the vapor incident flux. A 3-in. metallic tin disc with 99.99% purity was used as sputtering target. Pure argon (99.999%) and oxygen (99.999%) were used as sputtering and reactive gases, respectively. The flow rates of Ar and $O_2$ were controlled with a MKS mass flow meter and their pressures were measured by Pirani and Penning pressure gauges. The discharge was generated at a constant DC power of 400 W. The flow rates of Ar and $O_2$ were kept constant at 12 sccm and 48 sccm, respectively. The silicon wafers (100) substrates were prepared by ultrasonic washer with acetone, before loaded into the deposition chamber. The deposition time was fixed at 90 min. Then, the effect of oxygen plasma with varing plasma power from 100 W to 300 W on tin oxide ($SnO_2$) nanorods was studied.

The film crystalline structures were examined by a RIGAKU, TTRAX III X-ray diffractometer operating with a Cu-$K_{\alpha 1}$ source. The measurements were conducted from 20-60° incident angles. The morphology of the films was examined by using field emission scanning electron microscopy (FE-SEM), and atomic-force S-4700 Hitachi microscopy (AFM).

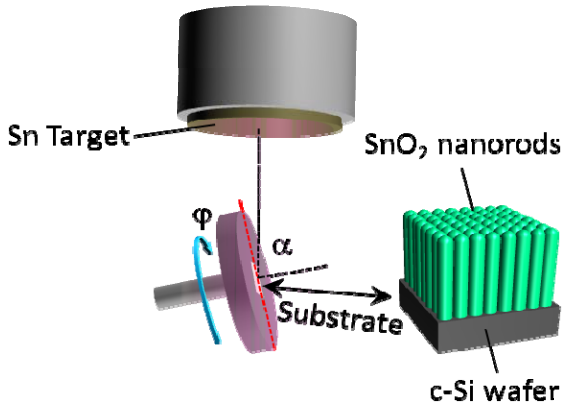


**Figure 1.** A schematic of GLAD with sputtering process

## 3. Results and Discussion

The crystal structure of tin oxide nanorod thin films with oxygen plasma power of 100 W to 300 W were revealed in a x-ray diffraction pattern as shown in Figure 2. It could be seen that the crystal structure of all $SnO_2$ nanorod films exhibited polycrystalline of $SnO_2$ tetragonal phase. The lattice spacings were calculated and compared to the JCPDS 88-0287. It was found that at high oxygen plasma power intense diffraction peak well crystalline were formed as shown in Table 1. The average crystalline size of $SnO_2$ nanorods calculated from the full-width at half maximum (FWHM) from XRD data by using the Scherrer's equation [10]. The variation of crystalline size is shown in Figure 2(b). The average crystalline size was slowly increased from approximately 3.7 nm to 4.2 nm as the oxygen plasma was increased power from 100 W to 300 W.

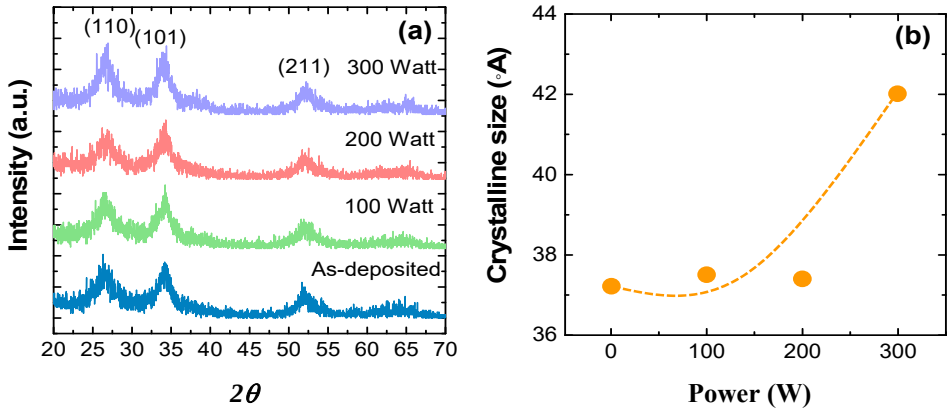


**Figure 2**. X-ray diffraction patterns of tin oxide nanorods with oxygen plasma power of 100 W to 300 W

**Table 1**. XRD peak position ($2\theta$) and lattice spacing ($d$) of the prepared $SnO_2$ nanorods after oxygen plasma treatment at different power

| Samples | (110) | | (101) | | (211) | |
|---|---|---|---|---|---|---|
| | $2\theta$ | $d_{hkl}$ | $2\theta$ | $d_{hkl}$ | $2\theta$ | $d_{hkl}$ |
| As-deposited | 26.53 | 3.36 | 34.03 | 2.63 | 52.09 | 1.75 |
| 100 W | 26.59 | 3.35 | 34.09 | 2.63 | 52.10 | 1.75 |
| 200 W | 26.68 | 3.33 | 34.07 | 2.63 | 52.18 | 1.75 |
| 300 W | 26.62 | 3.34 | 34.05 | 2.63 | 52.20 | 1.75 |

The SEM images of tin oxide thin films with oxygen plasma power of 100 W to 300 W are shown in Figure 3. It could be seen that the tin oxide thin films exhibited columnar nanorods structures. However, the nanorod structures of tin oxide with the lowest oxygen plasma power are relatively smaller and denser with smoother surfaces compared with other nanorod structures prepared at higher oxygen plasma powers. Then, the thickness of tin oxide nanorod thin films with highest oxygen plasma power were lower because the tin oxide nanorod thin films were scattered with oxygen plasma.

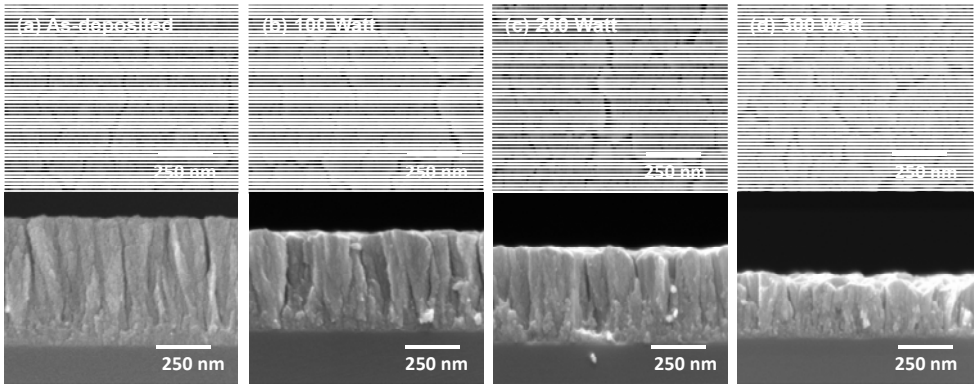


**Figure 3**. FE-SEM images of tin oxide nanorod thin films with oxygen plasma power of 100 W to 300 W

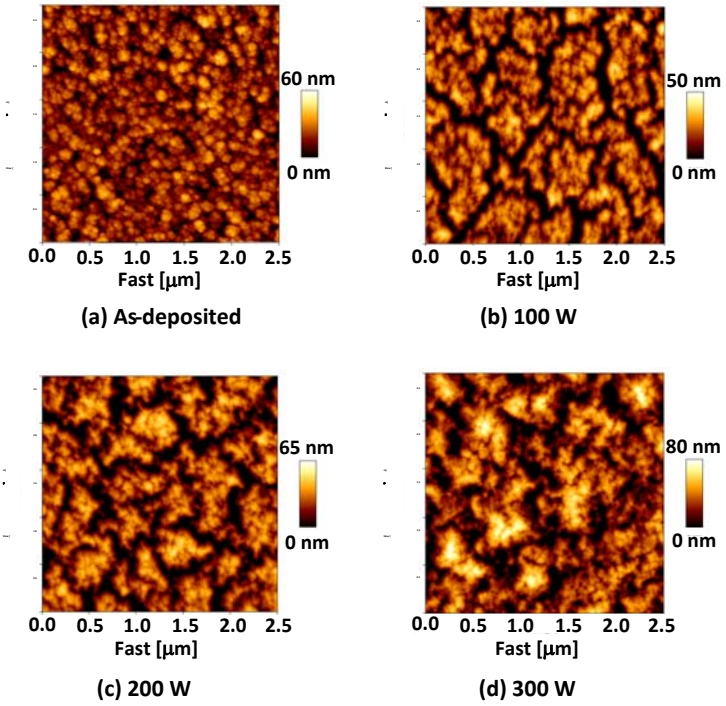


**Figure 4**. AFM images of tin oxide nanorod thin films with oxygen plasma powers of 100 W to 300 W

Figure 4 shows the AFM images of tin oxide nanorod thin films with oxygen plasma power of 100 W to 300 W From Figure 4, it could be seen that the surface roughnesses of tin oxide nanorod thin films with oxygen plasma power of 100 W to 300 W were 6.98 nm, 8.63 nm, 11.29 nm and 14.27 nm, respectively. It could be seen that the surface roughnesses of tin oxide nanorod thin films are increased with oxygen plasma power increasing.

## 4. Conclusions

In conclusions, well-aligned nanocolum $SnO_2$ nanorods were successfully fabricated via GLAD technique. The structure and moprphology of $SnO_2$ nanorods plasma treated with different power were studied. The as-deposited $SnO_2$ nanorod was orthorhombic phase and the crystalline size of $SnO_2$ nanorod slightly increased with increasing the oxygen plasma power while the oxygen plasma treatment did not affect the crystallinity of $SnO_2$ nanorods. However, the morphology of $SnO_2$ structure did not changed by reducing the thickness. The AFM analyses also indicated continuous increasing in the surface roughness when the power increased.

## References


[1] Gubbins, M.A., Casey, V. and Newcomb, S.B., **2002**. Nanostructural characterisation of $SnO_2$ thin films prepared by reactiver.f. magnetron sputtering of tin, *Thin Solid Films*, 405, 270–275.

[2] Wang, B., Zhu, L.F., Yang, Y.H., Xu, N.S. and Yang, G.W., **2008**. Fabrication of a $SnO_2$ nanowire gas sensor and sensor performance for hydrogen. *J. Phys. Chem. C*, 112(17), 6643–6647.

[3] Sharma, A., Tomar, M. and Gupta, V., **2011**. $SnO_2$ thin film sensor with enhanced responsefor $NO_2$ gas at lower temperatures. *Sens. Actuators B: Chem.*, 156(2) 743–752.

[4] Deniz, D., Frankel, D. J. and Lad, R. J., **2010**. Nanostructured tungsten and tungsten trioxide films prepared by glancing angle deposition. *Thin Solid Films*, 518, 4095–4099.

[5] LaForge, J. M., Taschuk, M.T. and Brett, M.J., **2011**. Glancing angle deposition of crystalline zinc oxide nanorods. *Thin Solid Films*, 519, 3530–3537.

[6] Horprathuma, M., Limwicheana, K., Wisitsoraatb, A., Eiamchaia, P., Aiempanakitc, K., Limnonthakuld, P., Nuntawonga, N., Pattantsetakula, V., Tuantranontb, A. and Chindaudom, P., **2013**. $NO_2$-sensing properties of $WO_3$ nanorods prepared by glancing angle DC magnetron sputtering. *Sensors and Actuators B*, 176, 685–691.

[7] Gwon, H.J., Moon, H.G., Jang, H.W., Yoon, S.J. and Yoo, K.S., **2013**. Sensitivity enhancementof nanostructured $SnO_2$ gas sensors fabricated using the glancing angledeposition method. *J. Nanosci. Nanotechnol.*, 13(4), 2740–2744.

[8] Oros, C., Horprathum, M., Wisitsoraat, A., Srichaiyaperk, T., Samransuksamer, B., Limwichean, S., Eiamchai, P., Phokharatkul, D., Nuntawong, N., Chananonnawathorn, C., Patthanasettakul, V., Klamchuen, A., Kaewkhao, J., Tuantranont, A. and Chindaudom, P., **2016**. Ultra-sensitive $NO_2$ sensor based on vertically aligned $SnO_2$ nanorods deposited by DC reactive magnetron sputtering with glancing angle deposition technique. *Sensors and Actuators B*, 223, 936–945.

[9] Du, H., Wang, J., Sun, Y., Yao, P., Li, X. and Yu, N., **2015**. Investigation of gas sensing properties of $SnO_2/In_2O_3$ composite hetero-nanofibers treated by oxygen plasma. *Sensors and Actuators B*, 206, 753–763.

[10] Cullity, B.D. and Stock, S.R., **2001**. Elements of X-ray Diffraction. 3rd edn. (Prentice Hall, New Jersey), p. 388.